COATING OF A POLYMER LAYER USING LOW POWDER PULSED

PLASMA IN A PLASMA CHAMBER OF A LARGE VOLUME

The present invention relates to the coating of surfaces, in
particular to the production of oil- and water- repellent
5   surfaces, as well as to coated articles obtained thereby.

Oil- and water- repellent treatments for a wide variety of
surfaces are in widespread use. For example, it may be
desirable to impart such properties to solid surfaces, such as
10   metal, glass, ceramics, paper, polymers etc. in order to improve
preservation properties, or to prevent or inhibit soiling.

A particular substrate which requires such coatings are fabrics,
in particular for outdoor clothing applications, sportswear,
15   leisurewear and in military applications. Their treatments
generally require the incorporation of a fluoropolymer into or
more particularly, fixed onto the surface of the clothing
fabric. The degree of oil and water repellency is a function of
the number and length of fluorocarbon groups or moieties that
20   can be fitted into the available space. The greater the
concentration of such moieties, the greater the repellency of
the finish.

In addition however, the polymeric compounds must be able to
25   form durable bonds with the substrate. Oil- and water-
repellent textile treatments are generally based on
fluoropolymers that are applied to fabric in the form of an
aqueous emulsion. The fabric remains breathable and permeable
to air since the treatment simply coats the fibres with a very
30   thin, liquid-repellent film. In order to make these finishes
durable, they are sometimes co-applied with cross-linking resins
that bind the fluoropolymer treatment to fibres. Whilst good
levels of durability towards laundering and dry-cleaning can be
achieved in this way, the cross-linking resins can seriously
35   damage cellulosic fibres and reduce the mechanical strength of
the material. Chemical methods for producing oil- and water-

2

repellent textiles are disclosed for example in WO 97/13024 and
British patent No 1,102,903 or M. Lewin et al., 'Handbood of
Fibre Science and Technology' Marcel and Dekker Inc., New York,
(1984) Vol 2, Part B Chapter 2.

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Plasma deposition techniques have been quite widely used for the
deposition of polymeric coatings onto a range of surfaces. This
technique is recognised as being a clean, dry technique that
generates little waste compared to conventional wet chemical
10 methods. Using this method, plasmas are generated from organic
molecules, which are subjected to an electrical field. When this
is done in the presence of a substrate, the radicals and
molecules of the compound in the plasma polymerise in the gas
phase and react with a growing polymer film on the substrate.
15 Conventional polymer synthesis tends to produce structures
containing repeat units which bear a strong resemblance to the
monomer species, whereas a polymer network generated using a
plasma can be extremely complex.

20 WO98/58117 describes the formation of oil or water repellent
coatings on a surface using monomeric unsaturated organic
compounds, and in particular unsaturated halocarbons, which are
polymerised on the surface using a plasma deposition process.
This process produces good oil and water repellent coatings, and
25 this is illustrated using small-scale units of 470cm^3.

For most commercial applications much larger scale production
units are required. However, initial trials revealed that
replication of the conditions used in the small-scale unit in
30 larger chambers did not produce satisfactory results.

According to the present invention, there is provided a method
for depositing a polymeric material onto a substrate, said
method comprising introducing an monomeric material in a gaseous
35 state into a plasma deposition chamber, igniting a glow
discharge within said chamber, and applying a voltage as a

pulsed field, at a power of from 0.001 to 500w/m^3 for a
sufficient period of time to allow a polymeric layer to form on
the surface of the substrate.

5   As used herein, the expression "in a gaseous state" refers to
gases or vapours, either alone or in mixture, as well as
aerosols.

These conditions are particularly suitable for depositing good
10   quality oil and water repellent surfaces of uniform thickness,
in large chambers, for example in chambers where the plasma zone
has a volume of greater than 500cm^3, for instance 0.5m^3 or more,
such as from 0.5m^3-10m^3 and suitably at about 1m^3. The layers
formed in this way have good mechanical strength and remain
15   substantially in place, through a conventional washing process.

The power levels, and particularly the power densities, that
give the best results are lower than those conventionally used
in this type of process. This is quite unexpected. In
20   particular the power is applied at from 0.001 to 100w/m^3,
suitably from 0.01 to 10w/m^3.

The dimensions of the chamber will be selected so as to
accommodate the particular substrate being treated, but in
25   general will be of a reasonably large size, to accommodate
plasma zones having the volumes described above. For instance,
generally cuboid chambers may be suitable for a wide range of
applications, but if necessary, elongate or rectangular chambers
may be constructed, for example where the substrates are
30   generally of this profile, such as wood, rolls of fabric etc.
Sheet materials can be processed using a "roll to roll"
arrangement.

The chamber may be a sealable container, to allow for batch
35   processes, or it may comprise inlets and outlets for substrates,
to allow it to be utilised in a continuous process. In

4

particular in the latter case, the pressure conditions necessary
for creating a plasma discharge within the chamber are
maintained using high volume pumps, as is conventional for
example in a device with a "whistling leak".

In particular, the monomeric material is a material as described
in WO98/58117. Specifically, it comprises an organic compound,
which comprises a chain of carbon atoms, at least some of which
are preferably substituted by halogen.

In particular, the compounds are unsaturated and so contain at
least one double bond or triple bond that is capable of reacting
to form a polymeric compound.   Preferably the compounds contain
at least one double bond.

By "chain" is meant that the carbon atoms form straight or
branched chains. Suitably, the chains are not cyclic. The
compounds used in the method of the invention include at least
one such chain. Suitable chains have from 3 to 20 carbon atoms,
more suitably from 6 to 12 carbon atoms

Monomeric compounds used in the method may include a double or
triple bond within a chain and so comprise an alkene or alkyne
respectively. Alternatively, the compounds may comprise an
alkyl chain, optionally substituted by halogen, as a substituent
which is attached to an unsaturated moiety either directly or by
way of an functional group, such as a ester or sulphonamide
group.

As used therein the term "halo" or "halogen" refers to fluorine,
chlorine, bromine and iodine. Particularly preferred halo
groups are fluoro. The term "aryl" refers to aromatic cyclic
groups such as phenyl or napthyl, in particular phenyl. The
term "alkyl" refers to straight or branched chains of carbon
atoms, suitably of up to 20 carbon atoms in length. The term

"alkenyl" refers to straight or branched unsaturated chains
suitably having from 2 to 20 carbon atoms.

Monomeric compounds where the chains comprise unsubstituted
5   alkyl or alkenyl groups are suitable for producing coatings
which are water repellent. By substituting at least some of the
hydrogen atoms in these chains these chains with at least some
halogen atoms, oil repellency may also be conferred by the
coating.
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Thus in a preferred aspect, the monomeric compounds include
haloalkyl moieties or comprise haloalkenyls. Therefore,
preferably the plasma used in the method of the invention will
comprise a monomeric unsaturated haloalkyl containing organic
15   compound.

Examples of monomeric organic compounds for use in the process
of the invention are compounds of formula (I)

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$$\underset{R^2}{\overset{R^1}{\diagdown}}C=C\underset{R^4}{\overset{R^3}{\diagup}} \qquad\qquad (I)$$
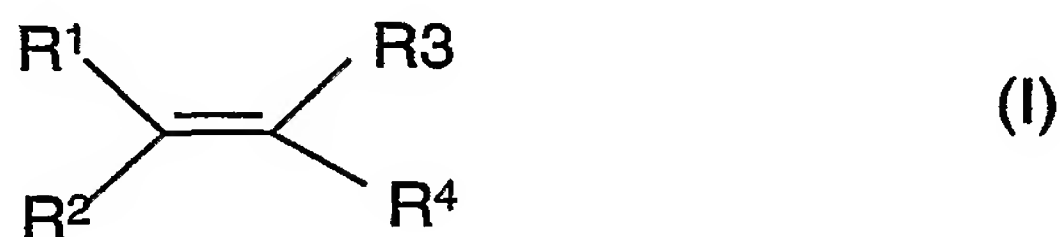
where R^1, R^2 and R^3 are independently selected from hydrogen,
alkyl, haloalkyl or aryl optionally substituted by halo;
25   provided that at least one of R^1, R^2 or R^3 is hydrogen, and
R^4 is a group X-R^5 where R^5 is an alkyl or haloalkyl group and X
is a bond; a group of formula $-C(O)O(CH_2)_nY-$ where n is an
integer of from 1 to 10 and Y is a bond or a sulphonamide group;
or a group $-(O)_pR^6(O)_q(CH_2)_t-$ where R^6 is aryl optionally
30   substituted by halo, p is 0 or 1, q is 0 or 1 and t is 0 or an
integer of from 1 to 10, provided that where q is 1, t is other
than 0.

6

Suitable haloalkyl groups for R^1, R^2, R^3 and R^5 are fluoroalkyl groups. The alkyl chains may be straight or branched and may include cyclic moieties.

5   For R^5, the alkyl chains suitably comprise 2 or more carbon atoms, suitably from 2-20 carbon atoms and preferably from 6 to 12 carbon atoms.

For R^1, R^2 and R^3, alkyl chains are generally preferred to have
10 from 1 to 6 carbon atoms.

Preferably R^5 is a haloalkyl, and more preferably a perhaloalkyl group, particularly a perfluoroalkyl group of formula C_mF_{2m+1} where m is an integer of 1 or more, suitably from 1-20, and
15 preferably from 6-12 such as 8 or 10.

Suitable alkyl groups for R^1, R^2 and R^3 have from 1 to 6 carbon atoms.

20 Preferably however, at least one of R^1, R^2 and R^3 is hydrogen and preferably R^1, R^2, R^3 are all hydrogen.

Where X is a group $-C(O)O(CH_2)_nY-$, n is an integer which provides a suitable spacer group. In particular, n is from 1 to 5,
25 preferably about 2.

Suitable sulphonamide groups for Y include those of formula $-N(R^7)SO_2^-$ where R^7 is hydrogen or alkyl such as C_{1-4}alkyl, in particular methyl or ethyl.

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In one embodiment, the compound of formula (I) is a compound of formula (II)

$$CH_2=CH-R^5 \qquad (II)$$

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where R^5 is as defined above in relation to formula (I).

In compounds of formula (II), X in formula (I) is a bond.

However in a preferred embodiment, the compound of formula (I)
is an acrylate of formula (III)

$$CH_2=CR^7C(O)O(CH_2)_nR^5 \qquad (III)$$

where n and R^5 as defined above in relation to formula (I) and R^7
is hydrogen, C_{1-10} alkyl, or C_{1-10}haloalkyl. In particular R^7 is
hydrogen or C_{1-6}alkyl such as methyl. A particular example of a
compound of formula (III) is a compound of formula (IV)

$$(IV)$$
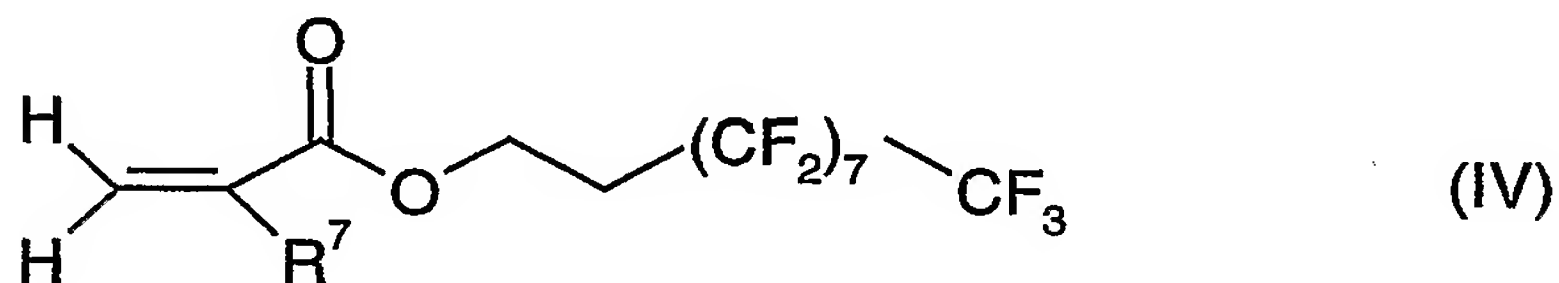
where R^7 is as defined above, and in particular is hydrogen and x
is an integer of from 1 to 9, for instance from 4 to 9, and
preferably 7. In that case, the compound of formula (IV) is
1H,1H,2H,2H-heptadecafluorodecylacylate.

Using these compounds in the process of the invention, coatings
with good water hydrophobicity and oleophobicity values are
achieved. These properties can be tested using "3M Test
Methods" such as the 3M oil repellency Test I, (3M Test Methods
Oct.1, 1988) and a water repellency test, (the 3M water
repellency Test II, water/alcohol drop test, 3M Test 1, 3M Test
Methods, October 1, 1998). These tests are designed to detect a
fluorochemical finish on all types of fabrics by measuring:

    (a) aqueous stain resistance using mixture of water
      and isopropyl alcohol.

    (b) the fabric's resistance to wetting by a selected series
      of hydrocarbon liquids of different surface tensions.

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These tests are not intended to give an absolute measure of the fabric's resistance to staining by watery or oily materials, since other factors such as fabric construction, fibre type,

5   dyes, other finishing agents, etc., also influence stain resistance. These tests can, however, be used to compare various finishes. The water repellency tests comprises placing 3 drops of a standard test liquid consisting of specified proportions of water and isopropyl alcohol by volume onto the

10   plasma polymerised surface. The surface is considered to repel this liquid if after 10 seconds, 2 of the 3 drops do not wet the fabric. From this, the water repellency rating is taken as being the test liquid with the greater proportion of isopropyl alcohol which passes the test. In the case of the oil

15   repellency test, 3 drops of hydrocarbon liquid are placed on the coated surface. If after 30 seconds no penetration or wetting of the fabric at the liquid-fabric interface occurs and no wicking around 2 of the 3 drops is evident, then the test is passed.

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The oil repellency rating is taken to be the highest-numbered test liquid which does not wet the fabric surface (where the increasing number corresponds to decreasing hydrocarbon chain and surface tension).

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The results obtained using these tests are variable depending upon the nature of the substrate, and in particular the roughness of the substrate, but certain products obtained using the method of the invention have achieved water hydrophobicity

30   values of up to 10 and oleophobicity values of 8 by means of large scale production. In fact, some coated materials has shown repellency to heptane and pentane, which represents a degree of oleophobicity which is off the normal 3M scale.

35   Other compounds of formula (I) are styrene derivatives as are well known in the art of polymerisation.

Suitable plasmas for use in the method of the invention include
non-equilibrium plasmas such as those generated by
radiofrequencies (Rf), microwaves or direct current (DC). They
5   may operate at atmospheric or sub-atmospheric pressures as are
known in the art. In particular however, they are generated by
radiofrequencies (Rf).

The gas supplied to the plasma chamber may comprise a vapour of
10 the monomeric compound alone, but preferably, it is combined
with a carrier gas, in particular, an inert gas such as helium
or argon. In particular helium is a preferred carrier gas as
this minimises fragmentation of the monomer.

15 The ratio of the monomeric gas to the carrier gas is suitably in
the range of from 100:1 to 1:100, for instance in the range of
from 10:1 to 1:100, and in particular about 1:1 to 1:10, such as
at about 1:5. This helps to achieve the high flow rates required
by the process of the invention.   Suitably the gas or gas
20 mixture is supplied at a rate of at least 1 standard cubic
centimetre per minute (sccm) and preferably in the range of from
1 to 100sccm.

Gases are suitably drawn into the chamber as a result of a
25 reduction in the pressure within the chamber as a result of a
evacuating pump, or they may be pumped into the chamber.

Polymerisation is suitably effected using vapours of compounds
of formula (I) in the chamber, which are maintained at pressures
30 of from 0.01 to 300 mbar, suitably at about 80-100mbar.

A glow discharge is then ignited by applying a high frequency
voltage, for example at 13.56MHz. This is suitably applied
using electrodes, which may be internal or external to the
35 chamber, but in the case of the larger chambers are preferably
internal.

The applied fields are suitably of power of up to 500W, suitably
at about 40W, applied as a pulsed field. The pulses are applied
in a sequence which yields very low average powers, for example
5   in a sequence in which the ratio of the time on : time off is in
the range of from 1:500 to 1:1000. Particular examples of such
sequence are sequences where power is on for 20μs and off for
from 1000μs to 20000μs. Typical average powers obtained in this
way are 0.04W.

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The fields are suitably applied from 30 seconds to 90 minutes,
preferably from 5 to 60 minutes, depending upon the nature of
the compound of formula (I) and the substrate etc.

15 Plasma polymerisation of compounds of formula (I), particularly
at average powers much lower than previously used, has been
found to result in the deposition of highly fluorinated coatings
which exhibit high levels of hydrophobicity and oleophobicity,
even when produced on a large scale. In addition, a high level
20   of structural retention of the compound of formula (I) occurs in
the coating layer, which may be attributed to the direct
polymerisation of the alkene monomer for instance a fluoroalkene
monomer via its highly susceptible double bond.

25 It has been noted, particularly in the case of the
polymerisation of compounds of formula (III) above, that low
power pulsed plasma polymerisation produces well-adhered
coatings which exhibit excellent water and oil repellency.
Furthermore, the coatings are of a good uniform thickness.

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The greater level of structural retention can be attributed to
free radical polymerisation occurring during the duty cycle off-
time and less fragmentation during the on-time.

35 The gas is suitably supplied to the chamber by way of a
temperature gradient. For example, gas is pumped along a heated

pipe leading from a gas supply to the plasma chamber. The pipe
is suitably heated such that the temperature of gas entering the
chamber is from 30 to 60°C, depending upon the nature of the
monomer used. In particular, the temperature of the gas

5   entering the chamber is higher, preferably about 10°C higher,
than the gas leaving the supply. The supply is suitably kept at
ambient temperature, or slightly elevated temperature such as
30°C, again depending upon the nature of the monomer involved.

10   Using heating of the supply pipes and chamber in this way, the
applicants have found that the monomer vapour is transported
efficiently into the chamber, and once in the chamber, remains
mobile. This leads to efficient deposition and polymerisation
of monomer, and minimises any condensation of gas, which may

15   occur in "cold spots" of the pipework. Although heating of the
chamber has been used previously in plasma etching processes in
order to keep etch products mobile, so that they can be
evacuated from the chamber, such a process is not required in
the present instance, and therefore it is unexpected that

20   heating is preferred.

Novel apparatus for use in the method described above, form a
further aspect of the invention. Specifically, the apparatus
comprises a plasma deposition chamber, a pumping system arranged

25   to feed monomer in gaseous form into the chamber, at least two
electrodes arranged so as to ignite a plasma within the chamber,
and power control means programmed to pulse power supplied to
the electrodes so as to produce a plasma at a power of from
0.001 to 500w/m^3 within a plasma zone within the chamber.

30

The pumping system is suitably one which can supply large
amounts of vapours into the chamber, and to ensure that this
remains in the chamber for the minimum adequate residence time,
to achieve the desired effect. It may comprise a series of

35   pumps, and large conductance pipes. The pumping system may also

be arranged to draw gas out of the chamber to evacuate air,
and/or reduce the pressure, as required.

In a particular embodiment, the pumping system comprises two
5   pumps. A first pump or roots pump, which is suitably a high
volume pump, is arranged to evacuate any vapours including water
vapour or other contaminants from the chamber. In order to do
this efficiently, and in a reasonable timeframe, bearing in mind
the size of the chamber, the pump is suitably arranged close to
10   the chamber, and connected to it by way of a single straight
pipe, with as large a diameter as possible. A valve is provided
in the pipe so that once the chamber has been evacuated, it can
be sealed.

15   A second pump is suitably a lower volume pump, such as a dry
rotary pump. This is suitably connected to the chamber by the
same opening as the first pump. It is arranged so that it can
draw monomer, together with any carrier gas into the chamber at
a suitable rate, and maintain the desired pressure and residence
20   time of gas within the chamber.

The pumping means suitably vents to a furnace where any
remaining monomer or fragments therefore, are incinerated before
the gases safely pass into the atmosphere.
25

Preferably the apparatus further comprises heating means for the
chamber. These may be integral with the walls of a chamber, or
present in a casing surrounding the chamber. They may comprise
electrical elements or recirculated, heated oil filled
30   elements, suitably under the control of a temperature
controller, to ensure that the desired temperature is maintained
within the chamber.

Preferably also the apparatus comprises a container for monomer,
35   which is connected to the chamber by a suitable pipe and valve
arrangement. Preferably, this container is provided with a

heater, which will allow the monomer to be heated above ambient
temperature, if required, before being introduced into the
chamber. Preferably the container, the pipe leading from it to
the chamber and the chamber itself are all heated, and the
5   heating means are arranged to produce an increasing temperature
gradient along the path of the monomer.

A supply of carrier gas may, if required, be connected to the
container and gas from this supply can be passed into the
10 container if required, in order to produce a sufficient flow of
gas into the chamber to produce the desired result.

In use, in a batch process, the items to be coated are
introduced into the chamber. In a particular embodiment, these
15 are ready made garments, to which a water and/or oil repellent
coating is to be applied. By depositing the polymer to the
finished garment, rather than to the fabric used in the
production, an "all over" coating is achieved, including areas
such as zips, fasteners or stitched joints, which would
20 otherwise remain uncoated.

The chamber is then evacuated, for instance using the entire
pump suite, but in particular the large roots pump where
provided. Once the chamber is evacuated, monomer vapour, which
25 is suitably warmed, is fed into it from the container. This is
achieved for instance, by drawing using a second pump from a
container in which a supply of liquid monomer is held. This
container is suitably heated to a temperature sufficient to
cause vaporisation of the monomer.
30
Preferably also the pipes and conduits which lead from the
container to the chamber are also heatable. This means that it
is possible to ensure that monomer is not lost through
condensation in the feed pipes.
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If desired, a carrier gas, which may be an inert gas such as argon or helium, and preferably helium may be fed through the chamber in order to provide a sufficient gas flow to achieve the desired concentrations and volume homogeneity of monomer in the 5   chamber.

Alternatively, monomer vapour may be drawn from the container and subsequently mixed with the carrier gas. Preferably prior to mixing, the monomer vapour is passed through a liquid/vapour 10   flow controller. This arrangement allows more controllable mixing to achieve the desired ratio of carrier gas : monomer. In addition, the environment of the monomer, and in particular the temperature, may be controlled independently of the flow requirements. Furthermore, reactive monomers may suitably be 15   stored in the container under an inert atmosphere for example, a nitrogen atmosphere. Suitably the container may be pressurised, so that the nitrogen is above atmospheric pressure, so as to assist the flow of monomer vapour from the container into the chamber, which is at lower pressure.
20

A glow discharge is then ignited within the chamber for instance by applying a voltage such as a high frequency voltage, for example at 13.56MHz. Thereafter, the power is pulsed as described above, so as to produce a low average power. As a 25   result, a monomer becomes activated and attaches to the surface of the substrate, whereupon it builds up a polymeric layer. At the low powers used in the method of the invention, unsaturated monomers form uniform layers of high structural integrity. The effect of this depends upon the nature of the monomer being 30   used, but the specific examples provided above can give excellent hydrophobicity and/or oleophobicity.

The invention will now be particularly described by way of example with reference to the accompanying diagrammatic drawings 35   in which:

Figure 1 is a diagrammatic representation of a monomer supply
system which can be used in an embodiment of the invention;

Figure 2 is a diagrammatic representation of a pumping system
5   which can be used in an embodiment of the invention; and

Figure 3 is a diagrammatic representation of alternative
apparatus which can be used in an embodiment of the invention.

10   The apparatus illustrated in Figure 1 shows a process system
containing a plasma chamber (1). Recirculated heated oil filled
heating elements are incorporated into outer walls of the plasma
chamber (1). The temperature within the chamber is measurable
by a thermocouple (not shown), and this information feeds to the
15   controls for the heater, so that the required temperature can be
maintained within the plasma chamber (1). Also within the
plasma chamber, a pair of facing electrodes are provided, which
define between them a plasma zone of approximately $1m^3$. The
electrodes are connected to a suitable power supply which is
20   controllable and programmable.

A monomer delivery pipe (3) which incorporates a valve (5) feeds
into the plasma chamber (1). A sealable chamber (7) for monomer
is provided at the end of the pipe (3). Within the chamber (7)
25   is arranged a support (9) on which an open container (11) for
monomer (13) can be positioned. The chamber (7) is provided
with a controllable heater, for instance a band heater (15),
extending around the chamber (7).

30   In addition, a supply of inert gas (17), such as argon or
helium, is connected to the chamber (7) by means of a pipe (19)
in which are provided a valve (21) and a manual valve (23)
together with a mass flow controller (25). The gas supply is
controllable and can be observed by means of a display (27).
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The plasma chamber (1) is provided with a pump arrangement
illustrated diagrammatically in Figure 2. This comprises a
roots and rotary pump combination, arranged to evacuate the
chamber. A roots pump (29) is connected to the plasma chamber
5   by means of a pipe (31) which is preferably straight and which
has as large a diameter as possible. In this case the diameter
of the pipe is 160mm. By ensuring that there are no bends in
the pipe (31), the conductance loss can be minimised. An
isolation valve (33) is provided in the pipe (31) so as to
10   isolate the pump (29) from the plasma chamber.

A low volume rotary pump (35) is also provided and is
connectable to the pipe (31) downstream of the valve (33), by
means of a smaller pipe (37), for instance of 63mm diameter,
15   provided with an automatic pressure control (APC) valve (39) and
an isolation valve (41). A flexible by-pass pipe (43), which is
also provided with a valve (45), connects the roots pump (29)
directly to the rotary pump (35).

20   Finally, a furnace (47) is provided downstream of the rotary
pump (35), which is provided so as to incinerate any gases
venting out of the system.

The combination of roots and rotary pump illustrated provides an
25   overall pumping speed of the order of 350m^3/hour, which allows
for rapid pumpdown of the plasma chamber.

An alternative arrangement is illustrated in Figure 3. In this
illustration, the electrodes (2) within the chamber (1) are
30   shown. These are electrically connected to an RF generator (4),
by way of an RF matching unit (6). The RF generator (4) is
controlled by a function generator (8) which is set to produce
pulses in the RF field as described above. The RF matching unit
ensures that the pulsing within the chamber (1) is in line with
35   that produced within the generator (4).

In this instance, the pump system is slightly different in that
the roots pump (29) and rotary pump (35) are interconnected by a
single 3-way process/roughing selector valve (40) that replaces
the valves 41 and 45 of the Figure 2 embodiment.   The pipe (37)

5   containing the process pressure control valve 39 also connects
to this valve.   As a result, the combination roots and rotary
pump can be used to draw gases through the process chamber (1)
and vent them to the furnace (47) in a broadly similar manner to
that described above in relation to Figures 1 and 2.   Rapid

10   evacuation of gas from within the chamber can be carried out by
opening valves 33 and 40 and operating the pump (29) and, if
required, also the pump (35).   However, the roots pump (29) can
be isolated from the system by closure of valves (33) and
adjustment of valve (40), and more controlled flow of gas

15   through the chamber induced by the use of pump (35), which draws
gas through pipe (37) when valve (39) is open.

In this apparatus also, the monomer feed arrangement is also
modified to make it more controllable.   Specifically, a separate

20   monomer handling unit (10) is provided.   This comprises a
monomer reservoir (12), in which monomer can be kept under
controlled environment conditions.   For instance, the monomer
can be kept in the dark, under an atmosphere of inert gas such
as nitrogen, which is supplied from a suitable gas supply (14).

25   These conditions minimise the chances that the monomer will
prematurely polymerise.

Monomer is able to feed out of the reservoir (12) through a pipe
(16) leading downwards from the monomer container (11) (not

30   shown in this instance).   This flow may be assisted by
maintaining the pressure of inert gas within the reservoir at
something above atmospheric pressure so as to create a pressure
differential.   A nitrogen bleed valve (32) is also provided in
the system.

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The pipe (16) suitably carries monomer into a liquid/vapour flow
controller (18) which is contained within a temperature
controlled gas unit (20). The temperature within the controller
(18) is monitored and controlled to ensure that any condensed
5   monomer is evaporated, and the vapour at the required
concentration leaves the controller via a valve (22), where it
enters a gas injector unit (24).

Within that unit, the monomer vapour is mixed with the required
10   amount of carrier gas, such as helium, which is fed into the
injector unit (24) from a suitable supply (17) by way of a
helium mass flow controller (26). Valves (28, 30) can be used
to isolate the helium supply (17) if required. The temperature
of the controller (26) can be independently controlled so that
15   gas at the appropriate pressure to achieve the desired mixture
is supplied to the injector unit (24). Mixtures produced in the
injector unit (24) are fed into the chamber (1) via pipe (3)
which is closable by valve (5) in a similar manner to that
described in relation to Figure 1.

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Example 1
A pillowcase was suspended within a plasma chamber of the
apparatus of Figure 1 and Figure 2, between the electrodes and
25   therefore within the plasma zone. In addition a sample of
1H,1H,2H,2H-heptadecafluorodecylacylate (10g) was placed into
the container (11) within the monomer chamber (7). At this time
the valves 5, 21, 23 and 33 are closed.

30   The plasma chamber was then rapidly (within 5 minutes) evacuated
to a pressure of 2×10^{-3} bar by opening valves 33 and 45, and
operating the pumps 29, 35 to draw air out of the chamber. The
rotary pump 35 was then isolated from the system by closing the
valves 33 and 45.

35

The plasma chamber was then heated by the heater in the walls of the process chamber (1) and a temperature of between 40-50°C, in particular 50°C was maintained.

5   Similarly the band heater 15 was operated to heat the monomer chamber 7 to a temperature of 45°C, and to maintain it at that temperature.

Valves 39 and 41 were then opened, as were valves 21 and 23, and
10   helium gas from the supply (17) was drawn into the chamber (7) by the operation of the rotary pump 35 at a rate of 60sccm. In passing over the monomer, the helium gas acted as a carrier to take monomer vapour into the plasma chamber.

15   After a period of 2 minutes, during which any remaining air was purged from the system, the desired pressure was reached within the chamber, and an RF plasma was ignited between the electrodes. The power supply was pulsed such that the power was on for 20µs and off for 20000µs.
20

Gases drawn through the plasma chamber were passed out through pipe 37 and pump 35, and into the furnace 47, which was held at 300°C.

25   After 30 minutes, the valves 39 and 41 were closed to isolate the pump 35, and the system was vented with dry nitrogen. The pillowcase was removed, the oil and water repellency tested using 3M oil repellency Test I, (3M Test Methods Oct.1, 1988) and a water repellency test, (the 3M water repellency Test II,
30   water/alcohol drop test, 3M Test 1, 3M Test Methods, October 1, 1998). The results, even after washing in a conventional washing machine, were water hydrophobicity values of 10 and oleophobicity values of 8.

In contrast, a pillowcase treated under similar conditions but with 200 watts of RF power at 13.56M Hz applied continuously produced a coating which was easily rubbed off.